

PATENT SPECIFICATION

NO DRAWINGS

996,193



996,193

Date of Application and filing Complete Specification July 6, 1961.

No. 24496/61.

Application made in Germany (No. L36505 IVc/81) on July 7, 1960.

Application made in Germany (No. H41314 IVa/23e) on Dec. 24, 1960.

Complete Specification Published June 23, 1965.

© Crown Copyright 1965.

Index at acceptance: —C5 D(6A1, 6A2, 6A4B, 6A5B, 6A5D1, 6A5D2, 6A5E, 6A5F, 6A7, 6A8A, 6A8B, 6A8C, 6A9, 6B1, 6B2, 6B4, 6B9, 6B10A, 6B10B, 6B11A, 6B11D, 6B12B1, 6B12B2, 6B12B3, 6B12E, 6B12F1, 6B12F2, 6B12F4, 6B12FX, 6B12G2A, 6B12G2B, 6B12G3, 6B12G4, 6B12G6, 6B12H, 6B12L, 6B12M, 6B12N1, 6B12N2, 6B12N3, 6B12N4, 6B12P, 6B13, 6C8, 6C10); D1 P(1A1B3, 1A1B4, 1A1B5, 1A3, 1A4, 1C2A, 1C3A, 1C3D, 1D)

Int. Cl.:—C 11 d/D 06 1

COMPLETE SPECIFICATION

Process for the Preparation of a Washing and Bleaching liquor for Textiles

We HENKEL & CIE G.M.B.H. a German Company, of 67, Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent 5 may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process of preparing washing and bleaching liquor for textiles and to a means whereby this process may be carried out.

Recently liquid washing and cleaning agents have become of increasing interest, due to the ease of measurement thereof, the simple pleasure packs and the rapid solubility of the agents, as compared with the powdered agents hitherto used. The usage, for example, for washing utensils or dishes, for domestic cleaning purposes, car washing, hair treatment, and fine and coarse disinfectant purposes, is being transferred more and more from the formerly popular powder product to the liquid concentrate. By liquid 25 concentrates of detergents is meant the normal commercially available concentrated solutions of dispersions of detergents which are dissolved in water to produce the solution—the washing liquid—in which a dirty article is washed. Generally, the term concentrate used in the specification means a solution or suspension needing considerable dilution to produce a wash liquor.

This development can be traced back to the advances in the unbreakable packing of liquid preparations and to the increasing use

of non-breakable plastic packs, which include both the known plastic bottles and plastic tubes closable by welding. Hitherto, only non-bleaching liquid washing and cleaning agents have appeared on the market, because the per-compounds necessary for the bleaching wash are not stable in alkaline solution; these, in combination with the other substances necessary for the washing and cleaning processes, are quickly decomposed in neutral medium, and particularly in alkaline medium, so that storage of such liquid concentrates is not possible.

The invention relates to a washing and bleaching process and to a process for the production of the washing and bleaching liquors required in the washing and bleaching process. The agent used in the process of the present invention consists of two flowable concentrates which are to be used together and which are packed separately, the first concentrate being neutral or acidic and containing the active oxygen carrier, together with stabilisers for the latter, and at least one non-oxidisable, acid-stable, organic, non-ionic and/or anionic detergent substance but containing no washing alkalis. The washing alkalis and other necessary or desirable substances for the washing process are contained in the second concentrate. By "flowable concentrates" are meant liquid or paste like solutions or dispersions prepared with use of a liquid, especially water, the viscosity of the solutions or dispersions being sufficiently low for them to flow under gravity from the opened package. By washing alkalis is

40

45

50

55

60

65

70

eric

67

3n

meant alkaline inorganic substances having surface-active properties. Such washing alkalis include certain carbonates, salts of the acids of phosphorus and of boron and alkali metal silicates is well known in the art.

Accordingly, this invention provides a process for the preparation of a washing and bleaching liquor for textiles, wherein the washing liquor is prepared by dissolving in water two aqueous liquid concentrates of which the first concentrate contains non-alkaline reacting percompounds required for carrying out the bleaching process, stabilisers for these per-compounds and at least one non-oxidisable acid-stable organic non-ionic and/or anionic detergent substance and the second concentrate contains washing alkalis as hereinbefore defined, the two concentrates being used in amount such that, after the concentrates have been dissolved in the washing liquor, said liquor possesses the alkalinity necessary for said washing and bleaching process.

In the first concentrate the active oxygen may be present in the form of more or less concentrated hydrogen peroxide solutions. These solutions may be formed by dissolving hydrogen peroxide in water. Alternatively the solutions may be formed by dissolving peroxyhydrates of alkali metal borates, alkali metal carbonates, salts of phosphorus acids (phosphates and phosphonates, the phosphates including not only the orthophosphates, but also the pyro-, meta- or poly-phosphates, especially the tripolyphosphates, and other condensed phosphates capable of forming peroxyhydrates), adducts of hydrogen peroxide to urea, or to the alkali metal salts of acetylation products of phosphorus acid described and claimed in British Patent Number 903,816. However, when the first concentrate is a dispersion the above peroxyhydrates may be present *per se*, as solids. This concentrate should not have an alkaline reaction, i.e. the pH value should not be greater than 7 and preferably not be greater than 6. Suitably acids which have a stabilising action on per-compounds, as for example phosphoric acid, are added in quantity such that the pH value of the perconcentrate amounts to at least 2 and preferably lies in the range 2.5 to 5.

For the adjustment of this concentrate to the desired pH value, there may be used, in addition to the already mentioned phosphoric acid, other acid-reacting substances, for example pyrophosphoric acid, sulphuric acid, acid alkali metal pyrophosphates, acid alkali metal orthophosphates and alkali metal bisulphates. Other acids, for example, hydrochloric acid, oxalic acid, benzoic acid, or lactic acid may also be used. Suitably such acids or acid salts are used which during the washing and bleaching process are neutralised and converted into active washing compounds. This applies primarily to phosphoric acid, pyrophosphoric acid, polyphosphoric acids and the acid salts or acid-reacting neutral salts of these acids. These phosphoric acids and their salts may also be used in the form of their hydrogen peroxide adducts.

These acid substances can be replaced by other, possibly non-acid stabilisers, or used jointly with other stabilisers, such as have already been proposed for the stabilisation of aqueous hydrogen peroxide solutions. Some of these other stabilisers are water-soluble compounds—especially those which are capable of forming complex salts with heavy metal ions—and some are water-insoluble substances of large specific surface area which are able to bind traces of heavy metals by surface adsorption. The water-soluble stabilisers include, for example, dipicolinic acid, quinaldic acid, quinolinic acid, acylation products of phosphoric acid (cf. British Patent No. 952373). Furthermore, complex-forming derivatives of mono- or poly-amines can be used of which the basic nitrogen atoms are substituted by lower residues containing carboxyl or hydroxyl groups, especially those of aliphatic or cycloaliphatic nature containing 1–6 carbon atoms, while several such residues may be linked to one nitrogen atom. These include, for example, substances of the type of ethylenediaminetetraacetic acid, nitrilotriacetic acid or monohydroxyethyl-ethylenediamine-triacetic acid. To the water-insoluble stabilisers belong various very finely divided solids with a large surface, such as silicic acid, alkaline earth metal silicates prepared by precipitation, especially magnesium silicate, and metastannic acid. Each of the two concentrates may contain a water-soluble component, which components, on mixing, react to form a water-insoluble stabiliser.

The acid-reacting per-condensate also contains non-oxidisable, i.e. saturated, organic basic washing agents stable to acids and of non-ionic and/or anionic nature, for example ethylene oxide adducts of fatty alcohols, alkyl phenols, fatty amines, fatty acids, fatty acid amides, fatty acid alkylolamides, and also condensation products of high molecular weight alkylsulphonic acids or alkylarylsulphonic acids with protein hydrolysates, acid-stable high molecular weight sulphonated acids of the aliphatic or mixed aliphatic-aromatic type, among which are also the further compounds mentioned below, provided they do not cause an alkaline reaction of the first concentrate.

It has proved that the above-mentioned non-oxidisable ethylene oxide adducts of fatty alcohols, or alkylphenols further surprisingly intensify the stabilising action of the acids or acid salts for active oxygen-containing compounds, so that the storability of the corresponding concentrate is improved. In

addition, anionic active substances stable towards acid exert an additional stabilising action, which however is inferior to that of the non-ionic compounds. The increased 5 stabilisation of the per-compounds by the said non-ionic or possibly by the anionic detergent substances is only observed, however, when the detergent substances have not been contaminated during their commercial 10 production by decomposition catalysts for per-compounds.

The second concentrate contains the washing alkalis and other substances not 15 present in the first concentrate but which are required for carrying out the washing process. These other substances include anionic and/or non-ionic detergent substances, which however may also possess wholly or partly unsaturated character, since a favoured oxidation thereof by the active oxygen during the washing and bleaching process is not deleterious. Besides the washing alkalis, additives to influence the foaming and dirt 20 carrying capacity of the washing liquid may be present in the second concentrate.

In addition to the substances already mentioned above, the remaining known anionic or non-ionic substances of natural or synthetic basis, or their combinations, may be 25 used as detergent substances, for example, soap, alkylbenzene sulphonates, fatty alcohol sulphates, fatty acid monoglyceride sulphates, fatty alcohol monoglyceryl ether sulphates or sulphonates or other sulphates of part esters of higher fatty acids with polyhydric alcohols or part ethers of higher fatty alcohols with polyhydric alcohols, for example, the fatty alcohol polyglycol ether sulphates. Moreover, fatty acid esters or fatty 30 alcohol ethers of hydroxy-sulphonic acids or hydroxy-carboxylic acids, or N-fatty acyl derivatives of aminosulphonic acids or amino-carboxylic acids can be used. The non-ionic detergent substances which can be used include the products of addition of ethylene oxide to fatty alcohols, fatty acids, part ethers of fatty alcohols part esters with polyhydric alcohols, products of addition of ethylene oxide to higher molecular weight 35 sulphonic acids or carboxylic acid amides. Products of addition of ethylene oxide to higher molecular weight polypropylene glycols can also be used.

As washing alkalis may be present in the 40 second concentrates the carbonates, ortho-, pyro- and poly-phosphates, silicates, especially metasilicates or alkali metal salts of weak organic acids, as for example alkali metal acetates, and combinations thereof.

These are used in such amounts that, after 45 mixing the alkaline concentrate with the preferably acid first concentrate, the mixture has a distinctly alkaline reaction (pH at least 7.5 or 8.5), which is necessary for the washing process depending on the material to be 50 washed and the conditions of washing. The pH value of the wash liquor should in general lie between 8 and 11 and preferably between 8.5 or 9 and 10. Caustic alkalis may also be added to increase the pH value of the second concentrates. For the rest, the concentrates are used in amount such that the content of active oxygen in the washing liquid lies in the range 20—200, preferably 40—90 mg/litre and the concentration of 55 organic detergent is up to 5, preferably 0.5—4 g/litre.

The second concentrates may contain substances which serve to increase the foaming power. Such substances are, for example, higher molecular weight carboxylic acid or sulphonate acid amides, (the amide nitrogen may be substituted, suitable substituents being primarily alkyl residues or polyglycol residues). In addition to the unsubstituted amides, the monoethanolamides and the reaction products of the unsubstituted amides with 1—5 mol of ethylene oxide may have proved useful. These substances may be derived from fatty acid amides, alkylsulphonic acid amides or alkyl-benzenesulphonic acid amides.

The washing agent concentrates according to the invention are of course intended preferably for operation in washing machines, where a high foaming power or a high stability of foam is undesirable. Therefore it is preferred to use weakly foaming detergent substance or to add substances which diminish the foaming power of the detergent substances employed. In this case it is advisable to use combinations of different types of detergent substances, which mutually interfere with one another in the development of foam. Such combinations are, for example, soap and synthetic substances of sulphate or sulphonate type, while the foaming power of these combinations of two may be further decreased by further additions of non-ionic surface-active substances. If surface-active polyethylene glycol ethers are used, an addition of products of addition of propylene oxide to surface-active polyethylene glycol ether soluble in water at room temperature has proved very satisfactory as a foam suppressor.

A combination which has proved especially useful is of surface-active polyethylene glycol ethers ($RO-EO-H$) with surface-active products of addition of propylene oxide to the said polyethylene glycol ethers ($RO-EO-PO-H$) in which the turbidity point of the polyethylene glycol ethers ($RO-EO-H$) is not over $60^{\circ}C.$, and is preferably in the range 30° to $45^{\circ}C.$, the turbidity point of the compound $RO-EO-H$ lies over that of the compound $RO-EO-PO-H$, and is preferably always greater than $60^{\circ}C.$, and 0.25 to 1.5, preferably 0.3 to 0.8 parts by weight of the compound $RO-EO-$

PO—H are present to one part by weight of the compound RO—HO—H.

These products of addition of propylene oxide to surface-active polyethylene glycol ethers may also be present in perconcentrates, especially in combination with surface-active ethylene glycol ethers which have no propylene glycol residues at the end of the polyether chain.

- 5 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 10 Different cations may also be used in admixture with one another, for example the sodium salts in admixture with the ethanolamine and/or morpholine salts.
- 15 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 20 Different cations may also be used in admixture with one another, for example the sodium salts in admixture with the ethanolamine and/or morpholine salts.
- 25 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 30 Different cations may also be used in admixture with one another, for example the sodium salts in admixture with the ethanolamine and/or morpholine salts.
- 35 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 40 Different cations may also be used in admixture with one another, for example the sodium salts in admixture with the ethanolamine and/or morpholine salts.
- 45 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 50 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 55 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The anionic detergent substances are advantageously used in the form of their readily soluble salts, e.g. of sodium or readily soluble organic bases, as for example in the form of the salts of mono-, di- or tri-ethanolamine or morpholine, then very concentrated pastes can be prepared.
- 60 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The remain-
- 65 In the production in flowable form of the concentrates to be used jointly according to the invention, a large variety of known procedures can be used. If hydrogen peroxide or its solutions are used as active oxygen carriers, no further measures are necessary; it is sufficient to add the water-soluble or water-insoluble stabilisers required to the hydrogen peroxide. Detergent substances are either readily soluble in water, or they are present in relatively concentrated form as pastes, so that here also there are no difficulties in converting them into flowable form. This applies particularly to the non-ionic active substances, of which most are miscible with water in all proportions. But the anionic substances also may be prepared in the form of aqueous pastes, for example 30% by weight of detergent. The remain-

ing washing alkalis may be incorporated in these pastes, wherein the washing alkalis may be hardly, partly or completely dissolved. The sodium salts of many anionic detergent substances are the more soluble, as are the potassium salts of the phosphates. It is advisable to use the more soluble salt. The quantities of sodium and potassium ions and the concentrations of the pastes are so adjusted that no undesired separation of the sparingly soluble salts takes place. Obviously all substances present in the alkaline concentrate may be present in the form of their salts with readily-soluble organic bases, such as mono-, di- or tri-ethanolamine.

In the production of the concentrates, especially the second, i.e. the alkaline concentrate, substances to aid solution can be used, and include, in addition to water-soluble organic solvents the so-called hydro-tropic substances of the type of toluene- or xylene-sulphonates. The latter may also be present in the form of their sodium and/or their potassium and/or their alkylolamine salts. Particularly useful water-soluble organic solvents are those with boiling points over 75°C., as for example the ethers of the same or different alcohols or the partial ethers of polyhydric and monohydric alcohols. These include, for example, di- or tri-ethylene glycols, polyglycerols and the partial ethers from ethylene glycol, propylene glycol or glycerine and aliphatic monohydric alcohols containing 1—4 carbon atoms. Also solvents, for example hydrocarbons, chlorinated hydrocarbons and alcohols which may often contribute to the production in liquid form and clarifying of the alkaline concentrate, are suitably introduced here.

Although the solubility of the water-soluble solids contained in the concentrates can be improved by the procedures described, the presence of such amounts of solids still in the concentrates which cause undesirable sedimentation cannot always be avoided. The sedimentation decreases with decreasing size of the solid particles, with a decrease in the difference between the specific gravities of the liquid and the solid suspended therein and with increasing viscosity of the liquid. While the sedimentation in many cases may be greatly diminished by a considerable lowering of the particle size of the suspended solids, in other cases good results are achieved by reducing the difference between the specific gravities of the solid and liquid, and increase of the specific gravity of the liquid is likewise sometimes advised. These measures can be combined as required.

In order to increase the specific gravity, addition of the above more precisely described hydro-tropic substances or suitable water-soluble organic solvents is advised. To increase the viscosity, addition of higher polyglycol ethers or polyglycerols, or other

water-soluble high molecular weight substances such as are used in the washing process as dirt carriers, is recommended. These include, for example, water-soluble salts of polyacrylic acid or polymethacrylic acid, which may be added to the active oxygen concentrate. Water-soluble derivatives of cellulose or starch, such as carboxymethylcellulose, ethers from cellulose and hydroxy sulphonic acids and cellulose sulphates may of course also be added to the alkaline concentrate, but are often not entirely soluble therein.

Finally, substances which activate the oxygen bleaching may be added to the alkaline concentrate. These include, for example, small quantities of heavy metal ions, especially copper ions. Since these ions may cause an undesirably rapid evolution of oxygen as decomposition catalysts for per-compounds, however, these activators must be used in bound form, i.e. either with excess amounts of complex-forming compounds, for example those of the type of the amine derivatives described in more detail above, or together with substances of large specific surface area, such as magnesium silicate. A combination of magnesium silicate, small amounts of copper and aminopolycarboxylic acids has proved useful as an activator.

Besides the compounds already mentioned in the acid and alkaline concentrates, there may be added to one or other of the concentrates as required further known inorganic basic washing substances, complex-forming compounds, solvents, thickeners, disinfectants, compounds with a dirt-carrying action, fibre or skin protecting agents, foam stabilisers, foam depressing agents, agents for protecting against corrosion, dyestuffs, optical brighteners, perfumes or mixtures of these substances or several of these substances together. The process will be effected so that, when putting into the acid concentrate, only such additives are co-employed which do not impair the stability of the compound containing active oxygen and moreover possess the necessary stability to acid. This is the case with some complex-forming compounds, disinfectants, agents for protecting against corrosion, dyestuffs and optical brighteners. In this connection may be mentioned polyphosphates as complex-forming compounds, bactericidal additives stable to acid such as formaldehyde, formic acid, and lactic acid, oxygen stabilisers such as proteins or their degradation products, water-soluble magnesium salts, condensation products of protein hydrolysates with higher molecular weight sulphonic acids, fatty acid methyl-turines, sulphonation products of imidazoline, polyvinyl alcohol or polyvinylpyrrolidone. Also certain agents for protecting against corrosion, such as say chromic acid, chromates or dichromates, may be put into the acid concentrate. Other additives, such as in particular alkali metal carbonates or silicates, thickeners of the type of polyacrylates, disinfectants of phenolic structure, dirt carrying agents such as alkali metal salts of carboxymethylcellulose, foam stabilisers such as fatty acid ethanolamides, some dyestuffs, brighteners and especially perfume compositions, on the other hand can only be put in the alkaline concentrate.

In each case it is necessary to ensure that the additives do not affect disadvantageously the stability and as far as possible also the homogeneity of the aqueous concentrates. These should possess the character of true or colloidal solutions or as far as possible stable suspensions. The perconcentrates may incorporate the further water-insoluble stabilisers mentioned above in non-homogeneous dispersed state.

The concentrates to be used jointly according to the invention may be packed in various ways. For use with washing machines wherein the two flowable concentrates may be supplied separately to a washing liquor, the concentrates may be packed in any way, preferably in bottles of flexible plastic material. However, small packages may also be produced, in which the concentrations are sealed by welding in plastic tubes in known way. In this type of packing the active oxygen concentrate may advantageously be closely associated with the alkaline concentrate. Thus, for example, a plastic tube can be divided by a welded seam into two parallel tubes filled with the concentrates to be used jointly. But there may also be provided one of the two tubes filled with concentrate together with the other concentrate in the second, correspondingly larger tube, so that this larger tube encloses both washing agent components.

Since it is often not advisable to expose the goods to be washed or the vessels to an acid treatment, the alkaline concentrate is usually first dissolved and then the acid concentrate. In the case of goods which are stable towards acid, as for example woolies, the procedure of course may also be reversed.

Simultaneous dissolving of the concentrates is also often advised. The concentrates may also be mixed before putting in and in this form are then dissolved to give the washing liquor. It is possible as a general principle either first to prepare a washing liquor and to put the goods to be washed into this, or to place the goods in the water and then to introduce the concentrates.

While with greater use of the concentrates, as for example in the laundries, the concentrates are suitably taken from relatively large barrels with corresponding control of weight, it is advisable in domestic use to employ two separate packages. These may be in the form of bottles, bags, sachets or any other

suitable form from which they can be simply removed. Glass, plastics, paper or cardboard impervious to liquid, metal or the like are suitable materials. The separate packages may be connected together, as for example, sachets made from seam-welded plastic tubes, double bottles, double bags. The division into the separate packages is effected with the condition that the acid and alkaline liquid concentrate in each case is contained in the one or other package in the quantity suitable for the carrying out of the washing process.

Thus, for example, for a washing process in a domestic drum washing machine, which is arranged for about 5 kg of dry washing, 200 g each of the concentrates according to Example 1 (acid) below and Example 4 (alkaline) below are required. Each of these concentrates is located in a polyethylene sachet, which are provided for use in the form of a double package, sometimes in seal-welded form. After charging the washing machine with the goods to be washed and the necessary quantity of water, the sachet with the alkaline liquid is first emptied into the drum, on which after a few revolutions of the drum, the acid concentrate from the other sachet is taken out and added to the washing liquor.

The introduction of the concentrates into the washing machine may also be effected by suitable dosing devices. In a domestic wash by the pot process the procedure is similar, it being suitable, especially in the case of heavily soiled washing, first to mix the washing liquor with the alkaline concentrate and then to introduce the goods to be washed, and after a sufficient time of action in the cold or with moderate warmth, to add the acid content rate, and to see that the desired pH value is attained by good mixing and oscillation. In machine laundering the procedure may also be similar, so that the washing process is divided into a preliminary washing process and a principal washing process.

According to the kind of goods to be washed, the pH value of the final washing liquor may be varied by alteration of the acid or alkaline agents in the two concentrates. While for most hot washing processes, especially for white, rough and coloured washing of cellulose textiles, final pH values between 8.5 and 10.5 have been found suitable, for fine washing processes, say for woollies, woven or knitted goods of chemical fibres, silk or rayon, and also for delicately coloured things, lower washing temperatures and a less alkaline washing liquor are preferred. In these cases, for example, pH values between 7.5 and 8.5 are used. Accordingly the acid and alkali dosings of the two concentrates should be adjusted.

The invention will now be further described by way of Examples. 65

In the following Examples the pH values were measured with glass electrodes and are given without correction. (For details relative to the accurate measurement of pH values in hydrogen peroxide solutions by means of glass electrodes refer to the publication by J.R. Kolczynski, E.M. Roth and E.S. Shanley, "Journal of the American Chemical Society", 1957, Vol. 79, pages 75 531—533.)

The acid perconcentrates described in the Examples 1 to 3 may be combined in any way with the alkaline concentrates of the Examples 4 to 7. On dilution of equal quantities of acid and alkaline concentrates with water, washing liquors of alkaline reaction are obtained the pH values of which lie between 8.8 and 9.5. 80

EXAMPLE 1. 85
5.5 parts by weight of acid sodium pyrophosphate, 0.3 parts by weight of potassium toluenesulphonate and 5 parts by weight of ethoxylated nonylphenol (having 13 ethoxy groups) are dissolved with heating in 60 parts by weight of distilled water. After cooling, 30 parts by weight of hydrogen peroxide (30%) are introduced with stirring. The acid concentrate has a pH value of 3.5. It may be filled into polyethylene bottles and retains its active oxygen content for months. 95

EXAMPLE 2. 100
In a way similar to that described in Example 1, 5 parts by weight of an ethoxylated coconut oil fatty alcohol (having 16 ethoxy groups), 0.3 parts by weight of potassium toluenesulphonate, 11 parts by weight of $K_2P_2O_7 \cdot 3.5H_2O$ and 21.3 parts by weight of hydrogen peroxide (30%) are dissolved in 60 parts by weight of distilled water. The adjustment to a pH value of 3.2 is effected by acidification with pyrophosphoric acid or sulphuric acid. This acid concentrate also is stable in plastic bottles or sacks for weeks without appreciable loss of oxygen. 105

EXAMPLE 3. 110
6 parts by weight of acid sodium pyrophosphate and 0.3 parts by weight of potassium toluenesulphonate are dissolved in 46 parts by weight of distilled water. Then 17 parts by weight of an alkylsulphonic acid-albumin condensate with 38% of active substance and 30 parts by weight of hydrogen peroxide (30%) are stirred in. The pH value of the acid concentrate amounts to 3.45. This product also is very stable. 115

EXAMPLE 4. 120
An alkaline concentrate is prepared from 50 parts by weight of distilled water, 15 parts by weight of a coconut oil fatty acid-

5 albumin condensate (sodium salt 36%), 19 parts by weight of a fatty acid methyl tauride (sodium salt 64%), 2 parts by weight of potassium toluenesulphonate, 25 parts by weight of a tetrapotassium pyrophosphate and 5 parts by weight of sodium metasilicate-9 hydrate. Finally 4 parts by weight of caustic potash are dissolved in the completely homogeneous, faintly opalescent solution. 65

10 EXAMPLE 5.

15 For the preparation of an alkaline concentrate, 15 parts by weight of a mixture of the potassium salts of a fat-albumin condensate and an alkylbenzenesulphonate (35% active substances), 10 parts by weight of fatty acid methyl tauride (sodium salt 64%), 2 parts by weight of potassium toluenesulphonate, 0.9 parts by weight of the tetrasodium salt of ethylenediamine-tetracetic acid and 20 25 parts by weight of tetrapotassium pyrophosphate are dissolved in 50 parts by weight of distilled water to give a homogeneous opalescent solution. This is adjusted to the required alkalinity with 3 parts by weight of 25 caustic potash. 70

15 EXAMPLE 6.

20 An alkaline concentrate contains dissolved in 56 parts of distilled water 5 parts by weight of a high molecular weight alkylsulphonate (sodium salt 80%), 10 parts by weight of a fatty acyl isethionate (sodium salt 60%), 2 parts by weight of potassium toluenesulphonate, 0.9 parts by weight of the tetrasodium salt of ethylenediamine-tetracetic acid and 18 parts by weight of tetra-potassium pyrophosphate. The adjustment of 25 the homogeneous opalescent solution to the desired alkalinity is effected with 4 parts by weight of solid caustic potash. 75

30 EXAMPLE 7.

35 For the preparation of an alkaline concentrate, 12.5 parts by weight of a triethanolamine salt of a dodecylbenzenesulphonic acid (40%), 6 parts by weight of a coconut oil fatty alcohol triethoxysulphate (sodium salt 35%), 10 parts by weight of an olein-potash soap (46% fatty acid), 3.4 parts by weight of the tetrasodium salt of ethylenediaminetetraacetic acid, 1.8 parts by weight of potassium toluenesulphonate and 5 parts by weight of solid caustic potash are dissolved in 50 parts by weight of distilled water, after which 8 parts by weight of methylcyclohexanol are stirred in. 80

40 WHAT WE CLAIM IS:—

45 1. A process of preparing a washing and bleaching liquor for textiles, wherein the washing liquor is prepared by dissolving in water two aqueous liquid concentrates of which the first concentrate contains non-alkaline reacting per-compounds required for carrying out the bleaching process, stabilisers for these per-compounds and at least 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125

one non-oxidisable, acid-stable organic non-ionic and/or anionic detergent substance, and the second concentrate contains washing alkalis as hereinbefore defined, the two concentrates being used in amount such that, after the concentrates have been dissolved in the washing liquor, said liquor possesses the alkalinity necessary for said washing and bleaching process. 65

2. Process as claimed in claim 1, in which the second concentrate is added to the washing and bleaching liquor before or after the introduction of the goods to be washed into the washing and bleaching liquor, provided the second concentrate is always added to the washing and bleaching liquor before the first concentrate. 70

3. Process as claimed in claim 1, in which the second concentrate is first dissolved in the bath, before or after the introduction of the goods to be washed into the washing liquor, the goods are introduced if necessary and are given a preliminary wash with the resulting alkaline bath, the first concentrate is added and the washing is completed. 75

4. Process as claimed in any one of claims 1—3, in which the concentrates preferably contain also one or more of the known complex-forming compounds, solvents, thickeners, disinfectants, compounds with a dirt-carrying action, fibre or skin protecting agents, foam stabilisers, foam-depressing agents, agents for protecting against corrosion, dyestuffs, optical brighteners, perfumes or mixtures of these substances or several of these substances together. 80

5. Process as claimed in any one of claims 1—4, in which hydrogen peroxide or perhydrates of salts of acylated phosphorous acid are used as active oxygen carriers. 85

6. Process as claimed in any one of claims 1—5, in which the first concentrate contains at least one water-insoluble stabiliser with a large specific surface area. 90

7. Process as claimed in claim 6, in which the water-insoluble stabiliser is magnesium silicate. 95

8. Process as claimed in any one of claims 1—7, in which the first concentrate contains a water-soluble stabiliser, preferably quinolinic acid, quinaldic acid, dipicolinic acid or an acylation product of phosphorous acid. 100

9. Process as claimed in any one of claims 1—8, in which the first concentrate possesses a pH value of 2—6. 105

10. Process as claimed in claim 9 in which the first concentrate has a pH value in the range 2.5—5. 110

11. Process as claimed in any one of claims 1—10, in which the second concentrate contains a stabiliser for the active oxygen carrier and/or fibre protecting agents. 115

12. Process as claimed in any one of claims 120

1—11, in which the second concentrate contains an activator for the per-compounds.

13. A process as claimed in any one of claims 1—12, in which each of the two concentrates contains a water-soluble component which components, on mixing, react to form a water-insoluble stabiliser for the active oxygen carrier.

14. Process as claimed in any one of claims 1—13, in which surface-active polyethylene glycol ethers, which may possibly contain propylene glycol residues, are present as detergent substances in the second concentrate.

15. Process as claimed in any one of claims 1—14, in which the second concentrate contains as organic detergent substances a combination of surface-active polyethylene glycol ethers ($\text{RO}-\text{EO}-\text{H}$) with surface-active products of addition of propylene oxide to the said polyethylene glycol ethers ($\text{RO}-\text{EO}-\text{PO}-\text{H}$), the turbidity point of the polyethylene glycol ethers ($\text{RO}-\text{EO}-\text{H}$) being not over 60°C . while the turbidity point of the compound $\text{RO}-\text{EO}-\text{H}$ lies over that of the compound $\text{RO}-\text{EO}-\text{PO}-\text{H}$ and in which case 0.25—1.5 parts by weight of the compound $\text{RO}-\text{EO}-\text{PO}-\text{H}$ are present to one part by weight of the compound $\text{RO}-\text{EO}-\text{H}$.

16. Process as claimed in claim 15, in which the turbidity point of the polyethylene glycol ethers lies in the range 30° — 45°C .

17. Process as claimed in claim 15 or 16 in which the turbidity point of the compound $\text{RO}-\text{EO}-\text{H}$ is greater than 60°C .

18. A process as claimed in any one of claims 15—17 on which 0.3—0.8 parts by weight of the compound $\text{RO}-\text{EO}-\text{PO}-\text{H}$ are present per one part by weight of the compound $\text{RO}-\text{EO}-\text{H}$.

19. Process as claimed in any one of claims 1—18, in which after dissolving the two concentrates the washing liquor has a pH in the range 8—11, a content of active oxygen of 20—200 mg per litre, and a content of organic detergent substance of up to 5 g. per litre.

20. Process as claimed in claim 19, in which after dissolving the two concentrates the washing liquor has a pH in the range 9—10.

21. Process as claimed in claim 19 or claim 20 in which the content of active oxygen in the washing liquor lies in the range 40—90 mg. per litre.

22. Process as claimed in any one of claims 19—21, in which the content of organic detergent substance in the washing liquor lies in the range 0.5—4 g. per litre.

23. Process for the preparation of a liquor for washing and bleaching textiles substantially as hereinbefore particularly described.

W. P. THOMPSON & CO.
12, Church Street, Liverpool, 1.
Chartered Patent Agents.